

Organic Nanopatterns studied by XPEEM

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INTRODUCTION

Nanostructures have attracted enormous interest during the past few years. Not only nanostructuring using lithographic techniques is intensely used, in particular in semiconductor science, but also self-organized nanostructures. In addition, the use of organic molecules has become an interesting field, since they offer a large variety of physical properties for potential use in electronic devices, like, e.g. field-effect transistors (OFETs), or organic light-emitting devices (OLEDs).

However, one of the basic problems with organic materials is the potential damage during conventional structuring techniques leading to, e.g. for OLEDs, drastically reduced quantum efficiencies. Instead, different techniques like printing or organic growth on nanopatterned substrates can be utilized. For the latter technique, the adsorption and chemical bonding of organic molecules plays an important role. On many metal substrates a strong covalent bonding of the organic molecules (in our case π -conjugated heteroaromatics) is observed, which in most cases leads to *flat-lying* molecules due to the strong π -interaction (as long as the bonding does not induce molecular fragmentation) which may induce even metastable phases. On Ag surfaces, *long-range ordered domains* can be observed [1], since the d-band, which is dominating the chemical interaction with the relevant molecular subunits, is well below the Fermi level. On *inert* substrates like e.g. SiO₂, Si₃N₄, NaCl or p(2x2)O/ Ni(111) [2], the comparatively stronger intermolecular interactions dominate the molecular arrangement leading to – in some cases – to *upright standing* molecules. Furthermore, self-organization in organic monolayers yielding stripe patterns with distances on the several 10 nm scale can be formed [3] which could be utilized for overgrowth and may thus induce nanopatterns in subsequently grown layers.

For our present studies we used two different kinds of substrates. First, periodic nanostructures of Au on SiO₂ (i.e. metallic reactive domains on an inert substrate) prepared by a colloidal self-arrangement technique [4] with a 2D period of 800 nm, and second, Au stripes formed on vicinal Si(100) with 1D periodicity and an average period of about 200 nm as derived from AFM and XPEEM (see fig. 2). BPDCA (benzo-2'5'1,12-perylene-1'6'-dicarboxylicanhydride) multilayer films (nominal film thicknesses ranging from 1 to several monolayers) were grown in-situ without further treatment of the ex-situ prepared substrates. XPEEM images and local NEXAFS spectra have been recorded at the PEEM2 of the Advanced Light Source (BL 7.3.3.1).

RESULTS

Fig. 1 shows a 2D XPEEM image recording the secondary electron emission after excitation at a photon energy of 541.5 eV from BPDCA multilayers on nanopatterned Au/SiO₂. The large area on the right side is due to a large Au domain, where no latex spheres have arranged prior to Au deposition. There is a clear intensity variation due to differences in the secondary electron signal. These variations are attributed to different molecular orientations: whereas in the Au-covered regions the molecules are oriented parallel to the substrate (due to the covalent bonding via the π -orbitals), there is a much stronger electron emission signal from areas where no Au is present, i.e. the molecules are oriented upright. This in turn means, that the patterning of the substrate is di-

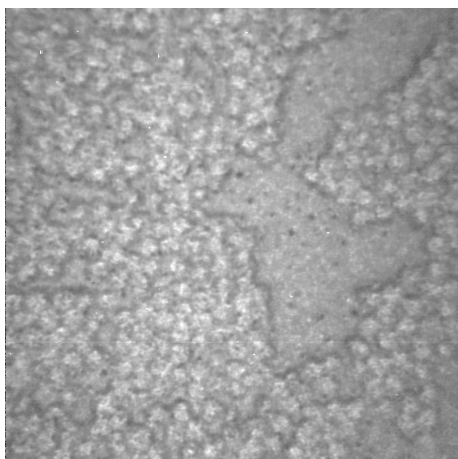


Fig. 1: XPEEM image from an in-situ prepared BPDCA film on a nanostructured substrate ($h\nu = 541.5$ eV; FOV: $15\ \mu\text{m}$).

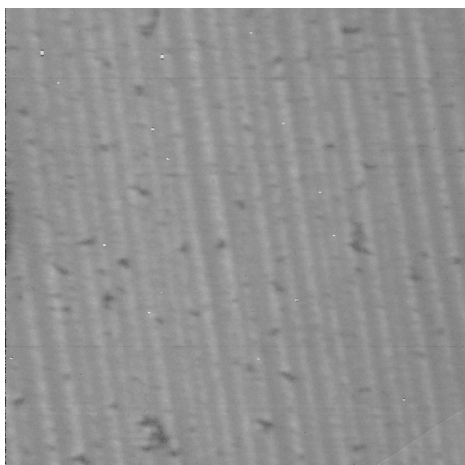


Fig. 2: XPEEM imaging of a thiol-SAM on Au nanostructures ($h\nu=700$ eV), which were prepared on vicinal Si prepared by a shadow mask technique.

rectly reflected in the molecular arrangement in the organic film. Note, that the lateral resolution of the present state-of-the art photoelectron emission microscopes (like PEEM2) do not allow to focus on the boundary between the differently oriented domains. It is of course of general interest to get insight on the molecular arrangement on a much smaller length scale to investigate domain boundaries on a molecular level. Scanning probe techniques like scanning tunneling microscopy fail due to the strong molecule-tip interactions. In addition, *local* structural information is needed to get insight into the lateral order within the domains. To answer these questions the next-generation spectromicroscopes (PEEM3) in combination with LEEM are thus of particular importance.

Fig. 2 shows another example of an organic film on a nanopatterned substrate: a thiol self-assembled monolayer has been adsorbed ex-situ. The image was recorded at a photon energy of 700 eV. At this energy, the contrast is mainly due to the high secondary electron emission from the Au-covered areas. A lateral resolution slightly better than 40 nm is derived from line scans using the conventional 15%-85% intensity argument. For lower energies, at e.g. the C K-edge, the signal-to-noise ratio is significantly worse and thus the lateral resolution is not sufficient to monitor variations in the secondary emission from differently oriented molecules. Subsequent experiments on BPDCA monolayers on the uncovered (no thiol preadsorption) thus yielded no significant contrast to unambiguously derive the pattern transformation from the substrate into the organic films.

Nevertheless, the present results clearly demonstrate the importance of a laterally resolving spectroscopic technique. Local NEXAFS spectra, in particular when used in

combination with high spectral resolution will become an routine tool to investigate the lateral inhomogeneities in soft matter films.

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